

NUMERICAL STUDY OF CARBON CLUSTER FORMATION IN PLASMAS WITH REGARD FOR CLUSTER CHARGES AND A BUFFER GAS INFLUENCE

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The theoretical analysis of processes which occur at fullerene formation in cooling carbon-helium plasma is fulfilled. In the presented theory most basic processes influencing on fullerene formation are taken into account.

The experimental detection of the new form of carbon, fullerenes, in 1985 [12] has offered new opportunities for both technology and fundamental physics. The unique shape of this molecule has led to the discoveries of interesting mechanical, chemical, and electrical properties of fullerenes and their derivatives. But the wide technological application of fullerenes and especially of their derivatives is constrained by the low efficiency of their synthesis. To increase this efficiency, it is necessary to develop the theoretical understanding of all processes occurring in a carbon-containing plasma upon the fullerene synthesis. It is already known [1, 2] that carbon cluster charges play an essential role in the process of fullerene formation. It is possible to alter the cluster charges in the plasma by influencing the electron concentration, for example by adding easily ionized metals.

The goal of this work is to study theoretically the fullerene formation in the plasma contained carbon clusters and buffer neutral gas (He). More precisely, we investigate the influence of plasma parameters (the electron concentration n_e and temperature T) and a buffer gas on the fullerene formation with regard for carbon cluster charges.

To develop a model, it is necessary to calculate the binding energies E_{bond} , ionization potentials IP_k , and electron affinities EA_k of different carbon clusters C_k by quantum-chemical methods. The calculations of these values for carbon clusters with different charges were carried out with help of the VASP [3] package for ab-initio calculations within the framework of density functional theory and pseudopotential approach.

In the model, we use the classical collision theory to calculate the collision cross section of two carbon clusters [4],

$$\sigma_{12} = \sigma_0(1 - E_{12}/\varepsilon_{\text{kin}}), \quad (1)$$

where $\sigma_0 = \pi r_{12}^2$ is the classical collision cross section of neutral clusters, $r_{12} = |r_1 + r_2|$ is the minimal distance between both clusters, r_1 and r_2 are the average sizes of these clusters, $E_{12} = q_1 q_2 / (r_1 + r_2)$ is the energy of Coulomb interaction of clusters with charges q_1 and q_2 and $\varepsilon_{\text{kin}} = 3/2 k_B T$ is the average kinetic energy of relative motion of both particles. From formula (1), one can see that the cross section of clusters with opposite charges may be far large than that for neutral clusters.

In the calculations, we considered the cluster charges to be only $\{0, \pm 1, -2\}e$ because, according of our calculations, all clusters C_k containing the number of atoms $k \in [1 - 80]$ with other charges have very high second ionization potential or negative third electron affinity. Using the Gibbs distribution, one can find that the probabilities for carbon clusters to exist with other charges are negligible at temperatures $T \sim 3000 \div 5000$ K.

As a basic assumption, we consider the carbon-containing plasma in a local thermodynamical equilibrium. So, the concentrations of all charged clusters may be found from the well-known Saha equations. In this case, the plasma temperature and electron temperature T_e are equal.

Earlier [5], we considered the formation of C_{60} and have found that there are the ranges of temperatures T and electron concentrations n_e , where the C_{60} formation rate is substantively greater than that at other T , n_e (Fig. 1). These ideas were developed for the calculation of the formation rate of endohedral fullerenes ($\text{Me}@C_{60}$), which also depends on temperature and the electron concentration [6]. The results of these calculations qualitatively correspond to our experimental results [7, 8]. But, in the models introduced above, the influence

of a buffer gas on the fullerene formation was not considered. In this paper, we develop an approach which allows one to take into account the buffer gas influence on the fullerene formation.

The approach is based on the consideration of a change of the carbon cluster concentrations n_k during the course of time. In this case, a scheme similar to that in [9] (the reduced description scheme) has been applied for the description of different carbon clusters and their behavior with the use of kinetic equations. According to this scheme, every cluster C_k is characterized, except for the number of atoms k in the cluster, by the number l of free radical bonds (dangling bonds) and by the cluster temperature T_k , which defines the rate of cluster oscillation excitation and which can differ from the plasma and electron temperature T_e . Values of T_k and T_e can differ during some time period Δt right after the new chemical bond formation in the cluster. Every C—C chemical bond formation in the cluster releases the energy $E_{\text{bond}} \cong 3.95$ eV, so this energy is distributed among all cluster's atoms, causing the increase in the cluster temperature T_k (oscillation temperature). So, this temperature would not be equal to the equilibrium plasma and electron temperature T_e , but the collisions of a cluster and buffer gas molecules (atoms) little by little will reduce the cluster temperature to $T_k = T_e$. Within the reduced description scheme, it is possible to describe not only the total concentration C_k at any time, but the partial concentration $n_{k,l,T}$ of any cluster C_k with l dangling bonds and temperature T_k as well.

We assume that the collision cross section of two clusters C_k and C_m in the reduced scheme depends not only on the numbers of atoms k and m , but on the numbers of radicals l_k and l_m in the clusters. We can expect that both clusters will be joined together if the piece of one cluster with a dangling bond will approach an analogous piece of another cluster at the distance r_b :

$$\sigma_{km}(l_k, l_m) = 4\pi r_b^2 l_k l_m (1 - E_{km}/\varepsilon_{\text{kin}}) P, \quad (2)$$

where $r_b \approx 1.7$ Å — effective distance of the interaction of two carbon atoms which leads to the formation of a chemical bond, $E_{km} = q_k q_m / (r_k + r_m)$ — energy of Coulomb interaction of these clusters with average sizes r_k and r_m , $P = \exp(-E_b/k_B T)$ — probability of the bond formation at a temperature T with the energy barrier E_b for the creation of a new carbon chemical bond. According to the results of [10], we take $E_b \cong 2$ eV.

For the synthesis of fullerenes in an electric arc, we consider that only the smallest clusters C_2 are

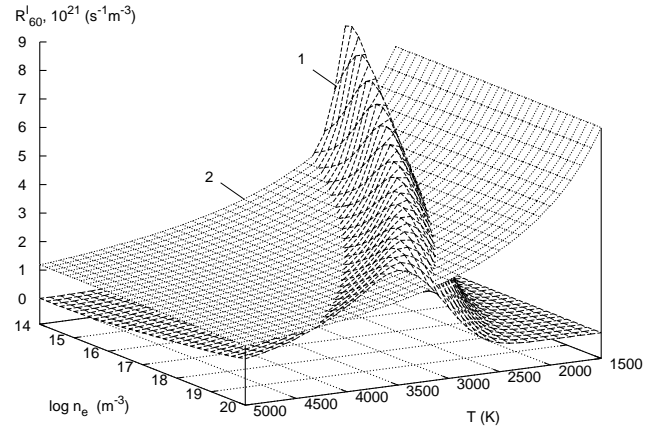


Fig. 1. Formation rate of C_{60} in one stage of reactions: 1 — with accounting the cluster charges, 2 — without accounting the cluster charges

evaporated from the carbon electrodes. This assumption was indirectly proved in [11]. Therefore, in the considered model, the initial conditions (namely at time $t = 0$) for the carbon cluster concentrations and temperature are

$$\begin{aligned} n_k(t=0) &= 0, n_2(t=0) = n_0, \\ T_2(t=0) &= T_e = 3000 \text{ K}. \end{aligned} \quad (3)$$

Then the concentration of C_2 is decreased in the fusion reactions running with the formation of bigger clusters. The concentrations of other clusters C_k are increased with the help of the fusion of two smaller clusters and are decreased by the reactions of C_k with other clusters.

The concentration $n_{k,l,T}$ of clusters C_k with k atoms, l_k radicals, and temperature T is increased upon the break of one bond in the cluster with the same number of atoms and with number of radicals $l'_k = l_k - 2$. In this case, the cluster oscillation temperature is decreased by $\Delta T = E_{\text{bond}}/2k$. On the other side, the concentration $n_{k,l,T}$ is decreased upon the formation of a new bond in the cluster. In this case, the oscillation temperature is increased by ΔT . Considering the processes of coagulations of two clusters having i and j atoms and different temperatures T_i and T_j , it is obvious that the oscillation temperature of a newly formed cluster is equal to $T_k = (iT_i + jT_j)/(i + j)$.

The frequencies of the breaking and formation of bonds are considered as proportional to the characteristic frequency of atom oscillations in carbon clusters, $\nu_{\text{vib}} \sim 10^{11} \text{ s}^{-1}$, which is considered as constant for all clusters.

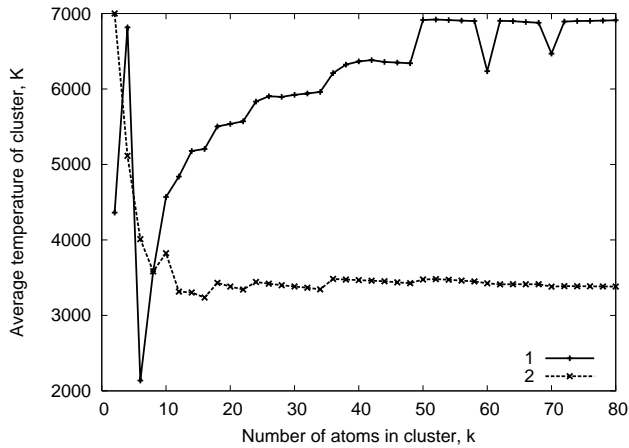


Fig. 2. Calculated average oscillation temperature $\langle T_k \rangle$ of every cluster C_k at the beginning of the computation, $t = 10^{-8}$ s (1); at the time of 6×10^{-7} s (2)

Taking into account all the reasons discussed above, the dynamic equations for the evolution of the concentration $n_{k,l,T}$ for all clusters C_k , $k \in [1 - 80]$,

$$\begin{aligned} \frac{d}{dt}n_{k,l_k,T_k} &= \sum_{i+j=k} \sum_{l_i} \sum_{T_i} \sum_{T_j} n_{i,l_i,T_i} n_{j,l_j,T_j} V_{ij} \sigma(l_i, l_j) - \\ &- \sum_{m=2}^{k_{\max}} \sum_{l_m} \sum_{T_m} n_{k,l_k,T_k} n_{m,l_m,T_m} V_{km} \sigma(l_k, l_m) + \\ &+ n_{k,l_k+2,T_k-\Delta T} \cdot \nu'_{\text{vib}} e^{-E_{\text{bar}}/k_B(T-\Delta T)} - \\ &- n_{k,l_k,T_k} \nu_{\text{vib}} e^{-E_{\text{bond}}/k_B T_k}, \end{aligned} \quad (4)$$

were solved by the numerical integration over time. Here, n_{k,l_k,T_k} — concentration of clusters C_k having l_k radicals and the oscillation temperature T_k , $V_{ij} = (8k_B T / \pi m_{ij})^{1/2}$ — relative velocity of the clusters i and j , m_{ij} — reduced mass of these clusters, and T — gas temperature. In the calculations, we took $T = 3000$ K and the initial conditions (3).

One of the basic lines of the proposed method is the accounting of the buffer gas influence on the heating and cooling of nonequilibrium carbon clusters. We consider that the oscillation energy of a cluster C_k is decreased by the rate

$$dT_k/dt = -\Delta E_{\text{He}} \nu_{\text{He}}, \quad (5)$$

where $\Delta E_{\text{He}} = -m_{\text{He}} \Delta V_{\text{He}}^2 / 2$ is the change of the helium atom kinetic energy upon the collision with a carbon cluster; $\nu_{\text{He}} = n_{\text{He}} V_{k,He} \sigma_{k,He}$ is the collision frequency of a cluster C_k with helium atoms, n_{He} is the buffer gas

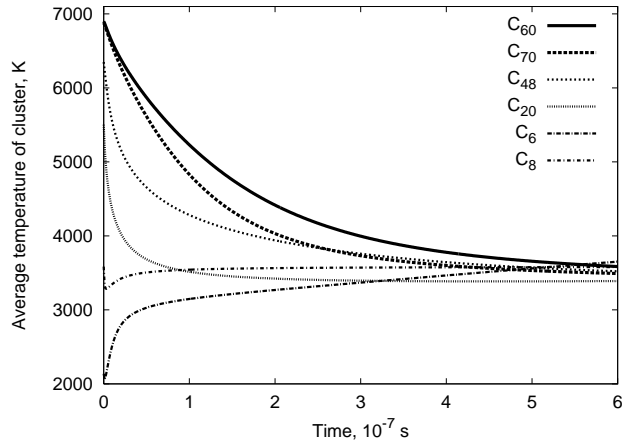


Fig. 3. Equalization of average cluster temperatures $\langle T_k \rangle$ during time steps

concentration; $V_{k,He}$ is the velocity of relative movement of a He atom and a cluster C_k ; and $\sigma_{k,He}$ is their collision cross section. $\Delta V_{\text{He}}^2 = \langle V_{\text{He}}^2 - (V'_{\text{He}})^2 \rangle$ is the change of the squared velocity of a helium atom before and after the collision which is averaged over the velocities of helium atoms; $V'_{\text{He}} = ((m_{k,He} - m_k) V_{\text{He}} + 2m_k V_{\text{eff}}) / (m_k + m_{\text{He}})$ is the velocity of a helium atom after the collision with a carbon cluster. $V_{\text{eff}} = \pm V_{\text{He}} \pm V_C$ is the relative velocity of a helium atom and a carbon atom of the cluster contacted with it. Upon the collision, the velocity of this carbon atom may be estimated as the total velocity $V_C = V_T \pm V_{\text{vib}}$, where $V_T = \sqrt{k_B T / m_k}$ is the average velocity of the cluster, and $V_{\text{vib}} = \sqrt{1/3 E_{\text{vib}} / m_C}$ is the characteristic velocity of oscillations of the cluster walls and $E_{\text{vib}} = ((3k - 6)k_B T_k) / (2k)$ is the average oscillation energy of the cluster per atom.

In Fig. 2, we show the average oscillation temperatures $\langle T_k \rangle$ of carbon clusters C_k at two different moments calculated at the beginning and at the end of the computation. Comparing curves 1 and 2 in Fig. 2, one can see that, in time about 10^{-6} s, the average oscillation temperatures of clusters distinctly decrease but these dependences become smoother. In Fig. 3, the dynamics of equalization of the average oscillation temperatures $\langle T_k \rangle$ for some carbon clusters is shown.

In Fig. 4, we show the cluster distribution by sizes at the end of the modeling time (6×10^{-7} s). The calculations give the total yield of C_{60} and C_{70} fullerenes about 20%. This value is overestimated as compared to the typical experimental yield. We assume that it is the result of disregarding the reactions of carbon cluster dissociation. For the same reason, a very high value of

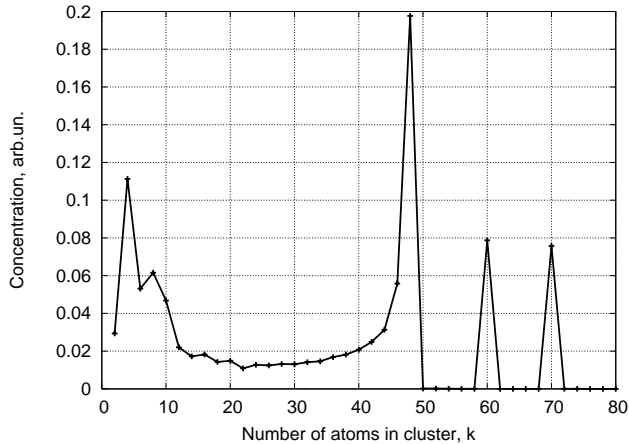


Fig. 4. Distribution of carbon clusters at the end of the fullerene growth. For the comparison, the experimental distribution of carbon clusters from [14] is shown by vertical lines

the C_{48} cluster concentration is obtained in the calculations. Also it may be explained by that, up to the cluster C_{48} , different cluster shapes (lines, rings, and open fullerene shells) are taken into account, but the bigger clusters are considered as open fullerene shells or fullerenes (C_{60} and C_{70}) only, according to the results of [13].

In addition, the proposed model does not take into account the strain energy of the cluster surface, so the smaller cluster concentrations would be overestimated.

In the given theory, the most basic processes influencing the fullerene formation are taken into account. Therefore in the future, we plan to define more precisely the theory of parameters to obtain a more accurate quantitative coincidence with experimental data obtained in different buffer gases.

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1. Afanas'ev D.V., Dyuzhev G.A., Karataev V.I. // Pis'ma Zh. Tekhn. Fiz. — 1999. — **25**, N5. — P.35–40.
2. Churilov G.N., Fedorov A.S., Novikov P.V. // Pis'ma Zh. Eksp. Teor. Fiz. — 2002. — **76**, N8. — P. 604–608.
3. Kresse G., Furthmuller J. // Phys. Rev. B. — 1996. — **54**. — P. 11169.
4. Landau L.D., Lifshits E.M. Mechanics. — Moscow: Nauka, 1973 (in Russian).
5. Churilov G.N., Fedorov A.S., Novikov P.V. // Carbon. — 2003. — **41**, N1. — P.173–178.
6. Fedorov A.S., Novikov P.V., Churilov G.N. // Chem. Phys. — 2003. — **293**, N2. — P. 253–261.
7. Churilov G.N., Alikhanyan A.S., Nikitin M.I. et al. // Pis'ma Zh. Tekhn. Fiz. — 2003. — **29**, N4. — P.81–85.
8. Churilov G.N., Weisman R.B., Bulina N.V. et al. // Fullerenes, Nanotubes and Carbon Nanostr. — 2003. — **11**, N4. — P.371–382.
9. Alekseev N.I., Dyuzhev G.A. // Zh. Tekhn. Fiz. — 1999. — **69**, N9. — P.104–109.
10. Strout D.L., Scuseria G.E. // J. Phys. Chem. — 1996. — **100**. — P.6492–6498.
11. Ebbesen T.W., Tabuchi J., Tanigaki K. // Chem. Phys. Lett. — 1992. — **191**. — P.336–338.
12. Kroto H.W., Heath J.R., O'Brien S.C. et al. // Nature. — 1985. — **318**. — P.162–163.
13. Hunter J.M., Fye J.L., Roskamp E.J. et al. // J. Phys. Chem. — 1994. — **98**. — P.1810–1818.
14. Rohlfing E.A., Cox D.M., Kaldor A. // J. Chem. Phys. — 1984. — **81**. — P.3322.

ЧИСЕЛЬНЕ ВИВЧЕННЯ УТВОРЕННЯ ВУГЛЕЦЕВИХ КЛАСТЕРІВ У ПЛАЗМІ З УРАХУВАННЯМ ЗАРЯДУ КЛАСТЕРА ТА ВПЛИВУ БУФЕРНОГО ГАЗУ

Г.Н. Чурилов, А.С. Федоров, П.В. Новиков, Ю.С. Мартинець

Резюме

Виконано теоретичний аналіз процесів, що супроводжують утворення фулеренів у холодній вуглець-гелієвій плазмі. Запропоновано теоретичну модель, що враховує більшість процесів, які впливають на утворення фулеренів.